

421.00

# NATIONAL BUREAU OF STANDARDS REPORT

9465

AD

Progress Report

INDUCED ACCELERATED DETERIORATION OF PORTLAND CEMENT CONCRETE

Semiannual Report

by

Raymond L. Blaine

9 January 1967



Chemical Research Laboratory  
RESEARCH LABORATORIES  
Edgewood Arsenal, Maryland 21010  
Contract D018-0-35-A6-02806

Sponsored by

BALLISTISTICS RESEARCH LABORATORIES  
Aberdeen Proving Ground, Maryland  
21005

NATIONAL BUREAU OF STANDARDS  
Washington, D. C. 20234



U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

see 9343

#### Distribution Statement

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTM: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010

#### Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

#### Disposition

Destroy this report when no longer needed. Do not return it to the originator.

# NATIONAL BUREAU OF STANDARDS REPORT

## NBS PROJECT

421.04-12-4212442

## NBS REPORT

9465

Progress Report

INDUCED ACCELERATED DETERIORATION OF PORTLAND CEMENT CONCRETE

Semiannual Report

by

Raymond L. Blaine

9 January 1967

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010

Chemical Research Laboratory  
RESEARCH LABORATORIES  
Edgewood Arsenal, Maryland 21010  
Contract D018-0-35-A6-02806

Sponsored by

BALLISTISTICS RESEARCH LABORATORIES  
Aberdeen Proving Ground, Maryland  
21005

NATIONAL BUREAU OF STANDARDS  
Washington, D. C. 20234

### IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS  
for use within the Government. Be  
and review. For this reason, the pr  
whole or in part, is not authorize  
Bureau of Standards, Washington, D  
the Report has been specifically pr

Approved for public release by the  
Director of the National Institute of  
Standards and Technology (NIST)  
on October 9, 2015

accounting documents intended  
jected to additional evaluation  
ting of this Report, either in  
ffice of the Director, National  
ie Government agency for which  
as for its own use.



U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS



## FOREWORD

The work described in this report was sponsored by the U.S. Army Ballistics Laboratories. This work was started in October 1965 and will continue for 18 months. Experimental data are contained in Vol. 1 of notebook dated October 1, 1965 assigned to R. L. Blaine.

## Notices

Reproduction of this document in whole or in part is prohibited except with permission of the CO, Edgewood Arsenal, Maryland 21010; however DDC is authorized to reproduce the document for United States Government purposes.

The information in this report has not been cleared for release to the general public.

## Acknowledgments

This research was supported by the US Army Ballistics Research Laboratories and was monitored by Edgewood Arsenal Research Laboratories, under Contract D018-0-35-A6-02806.



## DIGEST

Measurements and observations were continued during the second six-month period of the effect of various chemical solutions on mortar bars made of two portland cements. Measurements were also made of the effect of the more aggressive chemicals on concrete cylinders made of these cements, and studies were continued on the induced electrochemical corrosion of reinforcing steel in concrete.

Some of the mortar specimens immersed in the various chemical solutions failed in less than 2 weeks, whereas others indicated no weight loss, cracking, or reduction in fundamental resonance frequency in 6 months. The type of cement used, the proportions of cement to sand, and the moisture content of the specimens at the start of the test all appeared to be significant variables. Although the ammonium salts appeared to be the more aggressive, most, but not all, of the sulfates were deleterious to the specimens made of the Type I cement but had little effect on the specimens of the Type II cement.

A series of mortar specimens was placed on end in shallow concentrated salt solutions. The absorption, evaporation, and crystal formation in the portions of the specimens exposed to the air caused cracking and disintegration in some instances. Ammonium acetate had the most severe effect.

Some of the 3x6 inch concrete cylinders placed in some of the salt solutions failed in 2 weeks, whereas others indicated little or no effect after 24 weeks of immersion. The ammonium salts appeared most aggressive. The type of cement, quality of the concrete, and the moisture content of the specimens at the time of test also appeared to be significant variables.

Some of the 3x6 inch concrete cylinders with reinforcing rods inserted in the major axis exhibited cracks in less than 24 hours to 4 or 5 days when a 110-volt direct electric current was used to corrode the reinforcing rods. Two of the 7 specimens did not crack in 3 weeks but exuded corrosion products where the steel rod entered the cylinder. With 55 volt direct electric current, up to 7 days were required to form the cracks in the cylinders.





## TABLE OF CONTENTS

	<u>Page</u>
Introduction	9
Tests Conducted During the Second 6-Month Period	9
Mortar Bars Stored in Chemical Solutions	10
Results of Tests of Mortar Specimens Stored in Solutions	10
Mortar Bars Stored on End in Chemical Solutions	11
Results of Tests of Mortar Bars Stored on End in Chemical Solutions	11
Concrete Cylinders Stored in Chemical Solutions	11
Results of Tests of Concrete in Chemical Solutions	12
Electrochemical Corrosion of Reinforcing Steel in Concrete	13
Plans for Future Work	16
Table 2-1 Time for Failure or the Change in Resonance Frequency in 6 Months of 1:3 (cement to sand) Mortars Made of Type I Cement When Stored in Solutions of the Various Reagents.	17
Table 2-2 Time for Failure or the Change in Resonance Frequency in 6 Months of 1:5 (cement to sand) Mortars Made of Type I Cement When Stored in Solutions of the Various Reagents.	18
Table 2-3 Time for Failure or the Change in Resonance Frequency in 6 Months of 1:3 (cement to sand) Mortars Made of Type II Cement When Stored in Solutions of the Various Reagents.	19
Table 2-4 Time for Failure or the Change in Resonance Frequency in 6 Months of 1:5 (cement to sand) Mortars Made of Type II Cement When Stored in Solutions of the Various Reagents.	20
Table 2-5 Time for Failure, or Change in Dynamic Modulus in 18 Weeks of Mortars Made of Type I Cement When Stored on End in Shallow Concentrated Solutions of the Various Reagents.	21
Table 2-6 Time for Failure, or Change in Dynamic Modulus in 18 Weeks of Mortars Made of Type II Cement When Stored on End in Shallow Concentrated Solutions of the Various Reagents.	22
Table 2-7 Time for Failure, or Change in Resonance Frequency in 24 Weeks of 3x6 inch Concrete Cylinders Made of Type I Cement When Stored in Solutions of the Various Reagents.	23
Table 2-8 Time for Failure, or Change in Resonance Frequency in 24 Weeks of 3x6 inch Concrete Cylinders Made of Type II Cement When Stored in Solutions of the Various Reagents.	24
Table 2-9 Time of Cracking of 3x6 inch Concrete Cylinders Having 3/8 inch Reinforcing Rod in the Principal Axis With an Applied Direct Electrical Current.	25

## TABLE OF CONTENTS

Distribution List	<u>Page</u> 27
Document Control Data - R&D, DD Form 1437, With Abstract and Keyword List	

## INDUCED ACCELERATED DETERIORATION OF PORTLAND CEMENT CONCRETE

### INTRODUCTION

The need for further information on the relative aggressiveness of different chemicals on portland cement concrete was presented in the previous semiannual progress report, together with a description of the tests used in the present study. These consisted of a series of screening tests of the effect of various chemical solutions on mortar specimens made of two types of portland cement, each with two proportions of cement to sand, and each of these tested while still moist and after air-drying. Most of the specimens were completely covered with the solutions, but some were placed on end in 3 or 4 cm of more concentrated solutions of the various salts. Concrete specimens were also made for test after curing. Information on the chemical and physical properties of the cements, the proportions and properties of the mortars and concretes were presented in the first progress report together with the test methods employed.

The results obtained when immersing the mortar-bar specimens in the more aggressive solutions for six weeks were presented in the previous report. It was reported that ammonium salts appeared to be the most aggressive, and specimens made of the Type II cement were more resistant to attack than those made of Type I cement. The mortars with the greater proportions of cement appeared more resistant to attack than the leaner mortars. Exploratory test results were also presented on the use of direct electric current to corrode reinforcing steel in concrete.

### Tests Conducted During The Second 6-Month Period

During the second six-month period, the measurements of the 4x4x16 cm mortar specimens stored in solutions of the various chemicals have been continued on a less frequent basis. A few additional reagents were obtained and their effects evaluated.

Measurements were continued on the effect of selected concentrated salt solutions on mortar specimens placed on end in 3 to 4 cm of the solutions allowing evaporation from the upper parts of the specimens.

The 3x6 inch concrete cylinders were placed in various salt solutions and measurements made of the amount of deterioration. A few additional tests have been made of the electrochemical corrosion of reinforcing rods in concrete cylinders.

### Mortar Bars Stored in Chemical Solutions

The chemical reagents used in these tests are listed in Table 2-1. Some reagents are in addition to those listed in the previous report. The oleic acid was used as received and was not diluted. The 3-pound quantity used did not cover the specimens. With the other reagents, 1 pound was dissolved in about 2700 ml of water, and 8 specimens (one from each of the variables) were placed in each of the solutions. Measurements were made of the fundamental resonance frequency prior to, and at various times after storage in the solutions for periods up to 6 months. The fundamental resonance frequencies of the specimens stored in the solutions of the reagents listed in the previous report have also been determined, some for a period of 9 months. When obvious failure occurred prior to these times, these specimens were removed from the solution and water added to cover the remaining specimen. This caused the solution to be more dilute than at the start of the test. Another factor causing dilution was the tendency of some of the salts to crystallize on the sides of the containers and the crystals force themselves out of the container.

### Results of Tests of Mortar Specimens Stored in Solutions

A tabulation of the results obtained up to the time of the 24 week measurements (20 weeks in 5 instances) of mortar specimens stored in the solutions are presented in Tables 2-1, 2-2, 2-3, and 2-4. The solutions of ammonium salts appeared to be the most deleterious. The richer 1:3 (cement to sand) mortars were generally more resistant to attack than the leaner 1:5 (cement to sand) mortars. The specimens made of the Type II cement were more resistant to attack than those made of the Type I cement. This was especially true with the sulfate salts. All of the sulfate salts were not equally aggressive. There were a number of instances where the air-dried specimens had greater resistance to the salt solutions than those placed in the solutions when moist. The reactive sulfate solutions usually caused checking and cracking of the surfaces of the specimens and in some instances noticeable expansions especially with the Type I cement mortars. Some badly checked specimens had very little reduction in the resonance frequency. The citric and lactic acids had a severe surface attack on the specimens and mold-like materials formed on top of the solutions in the containers. Voluminous quantities of white reaction products were formed. The reaction of the oleic acid was not so severe but there was considerable attack and the acid became very viscous.



In some instances there was a more or less regular reduction in the resonance frequency with time whereas in other instances very little effect was noted until large cracks occurred in the specimens. In some solutions the specimens sloughed badly whereas in others there was no evidence of surface attack but the resonance frequency decreased.

#### Mortar Bars Stored on End in Chemical Solutions

Mortar bar specimens were stored on end in 3 or 4 cm of selected chemical solutions allowing evaporation of solutions and crystal growth on the upper portion of the specimens exposed to laboratory air. For these tests, the selected reagents listed in Table 2-5 and 2-6 were used. One pound of each reagent was mixed in 500 ml water and 8 specimens (one of each of the variables) placed on end in each of the solutions. Only 4 specimens, all air dried, were placed in the ferric ammonium sulfate solution. Measurements were made of the fundamental resonance frequency just prior to, and at intervals after being placed in the solutions. Observations were also made of cracks in the specimens.

#### Results of Tests of Mortar Bars Stored on End in Chemical Solutions

A tabulation of the results obtained up to 18 weeks on the mortar bar specimens stored on end in 3-4 cm solutions are presented in Tables 2-5 and 2-6. In some instances the specimens readily absorbed the solutions and large quantities of crystals were formed on the specimens. In other instances the specimens appeared moist for a very limited distance from the tops of the solutions, and some specimens appeared to be attacked only in the solutions. The action of the ammonium acetate appeared to be the most severe. Some of the mortar specimens in concentrated ammonium sulfate, ammonium nitrate and calcium chloride solutions also failed in relatively short periods. The differences in effectiveness of the different salts when the specimens were completely immersed (Tables 2-1, 2-2, 2-3, and 2-4), and when placed on end in the solutions of these chemicals (Tables 2-5 and 2-6) may be attributed in part to the crystal growth within the specimens, and in part to the fact that the latter solutions were more concentrated. The differences in chemical composition of the cements did not appear to have so great an effect when specimens were placed on end in solutions as when they were completely immersed.

#### Concrete Cylinders Stored in Chemical Solutions

The 3x6 inch concrete cylinders made of the 2 types of cement and of two qualities were stored in 95 to 100% RH for 28 days. Half of each of the specimens made of mix A and mix B was then transferred to laboratory air at 50% RH. The mix C specimens remained in the high humidity

storage until tested. At the age of about 4 months for specimens made of mixes A and B and 3 months for specimens made of mix C the cylinders were placed in solutions of various chemicals listed in Table 2-7. The solutions consisted of 1 lb of the reagent in approximately 2700 ml water. Three specimens were placed in each container. Water was added from time to time to replace that lost by evaporation. The weight and fundamental resonance frequency was determined prior to, and at intervals after immersion in the various solutions. Only six of the cylinders were immersed in the ammonium acetate solution, the other 3 being placed in a shallow (3 to 4 cm) concentrated solution of the salt.

#### Results of Tests of Concrete in Chemical Solutions

A tabulation of the results of the tests on the concrete cylinders stored in the various chemical solutions up to 24 weeks are presented in Tables 2-7 and 2-8. A reduction in fundamental resonance frequency of 1600 cps was used as an indication of failure. Some of the specimens, especially those made of the Type I cement stored in the sodium, potassium or ammonium sulfate solutions, failed by spalling. The bottom edges of the cylinders expanded and curled outward and in some instances the pieces broke away from the cylinder. The resonance frequency could not be determined accurately after this condition occurred. The effects of the solutions of the various reagents on the concrete cylinders were, in most but not all instances, similar to the effects on the mortar specimens which were immersed in the solutions. The three concrete cylinders placed on end in 3 to 4 cm concentrated ammonium acetate solution became soft below the top level of the solution and some material sloughed off within a few days. Crystals formed on the sides of the cylinders and in one week the crystals of the Type I cement, B mix had reached the top of the cylinder. The crystals were about half way up on the cylinders made of the A mix and Types I and II cement. The crystals and soft spongy concrete was scraped off and returned to the solution and this was repeated the second week. Judged by weight loss and appearance, the more porous "B mix" specimen had the most severe damage, but this appeared limited to the surface of the cylinder and the core appeared fairly firm. After these measurements, the cylinders were returned to the solution and crystals again formed on the parts of the cylinders above the solution. Water was added from time to time taking care not to wash any of the salt crystals back into the solution. There was not apparent further action when the crystals were not redissolved.

## Electrochemical Corrosion of Reinforcing Steel in Concrete

A number of exploratory tests were made to test the feasibility of using direct electric current to cause sufficient corrosion of the reinforcing steel in concrete so that splitting or cracking of the specimens would occur.

Some preliminary tests were made using 2x4 inch mortar cylinders made of 1:3 cement to sand. Small reinforcing rods were placed in the principal axis of the cylinders when made. These rods were inserted to about two thirds of the depth of the mortar and extended 2 inches or more above the tops of the cylinders.

Concrete cylinders (3x6 inches) were also made of the Types I and II cements using mixes A, B and C as previously described. The rods were vibrated into place as above, and cured in moist air, after which some cylinders were dried in laboratory air. Some 6x12 inch concrete cylinders were made using the Type I cement and mix A. Two different sizes of reinforcing rods were used in these cylinders.

In making the tests, the positive lead of the dc potential was connected to the reinforcing rod at the top of the cylinder, and the negative lead connected to a bronze screen wire or to another reinforcing rod in the liquid in which the cylinder was placed. Under these conditions, oxygen ions go to the reinforcing rod in the concrete (the anode) and the hydrogen to the cathode in the liquid or electrolyte outside the specimens. Potentials of 110, 55 and 18 volts were used. Because of the electrical resistance of concrete it was at first believed necessary to add salts to the surrounding water and to have the solution within a half inch to 1 inch from the top of the specimen. Later tests were made using only tap water with no added electrolytes, and in some instances with lesser depth of immersion of the specimens. Some measurements were made of the amount of current at different times. Observations were also made of the time of cracking and of the extrusion of the corrosion product. Some of these observations are presented to indicate more clearly some of the variables involved and the problems associated with the corrosion of the steel.

The first tests were made on 1:3 (cement to sand) cylinders with 1/4 inch and 3/8 inch reinforcing rods. With 110 volts direct current, a moist cured cylinder in NaCl solution in a small beaker formed a hair-line crack in about 1 hour. The crack extended from the rod on top of the cylinder and down one side. The temperature of the electrolyte went up to 95°C. The crack did not open appreciably with an additional 5 hours of applied voltage. The cylinder was split open, and the brown corrosion



product was found in the crack in the cylinder as well as on the reinforcing rod and in the mortar in the opposite side of the cylinder from that where the crack appeared.

Another wet 2x4 inch cylinder with a 3/8 inch reinforcing rod was placed in NaCl solution and 110v dc used. Gas and water bubbled out of the top of the specimen near the reinforcing rod and later a yellowish brown corrosion product. The temperature of the electrolyte went up to 98°C and after 2 hours it was down to 80°C. The specimen cracked in less than one hour. The current was turned off, and the following morning again turned on. The corrosion product came out into the electrolyte and the crack opened to about 1 mm on one side of the cylinder.

A wet 3x6 inch concrete cylinder made of the Type I cement, mix A, was placed in NaCl solution with 18 volts dc potential. The current was 0.13 amperes at the start but decreased to 0.10 amps in 2 hours and 0.06 amps in 8 days. No visible cracks were found in 2 weeks. The corrosion product all came out at the top of the cylinder near the reinforcing rod and, being rather fluid, ran into the electrolyte. At 14 days the electrolyte was filtered and 7 grams dried blackish brown solids recovered.

In another test, a 3x6 inch concrete cylinder in  $\text{CaCl}_2$  solution had a very rapid electrolytic reaction at the start but the action had come to a complete stop in 3 hours. The cathode had become coated with a white materials, (possibly lime) and when replaced, the action became rapid again. In this cylinder, the corrosion product came out in two places on the side of the specimen. No crack could be seen at the time the test was stopped. The cylinder was broken open and path of the corrosion product from the rod to the outside of the cylinder noted.

A 3x6 inch cylinder in an ammonium chloride solution, and using an 18 volt potential, had a current of 0.14 amps at the start of the test. Two days later, the current was 0.09 amps after which it increased to 0.13 amps. The cylinder was not removed until 10 days after the test was started. At that time horizontal cracks were noted near the bottom of the cylinder. Twelve grams of corrosion product in the electrolyte in the container was recovered by filtration.

With a 3x6 inch cylinder in calcium chloride solution, and using an 18 volt potential, the cathode became coated and the current, originally 0.14 apms, went down to 0.06 amps. Replacing the cathode caused an increase in the current to 0.09 amps. At 7 days, horizontal cracks in the cylinder were observed.



Other salts such as  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaHCO}_3$  and  $\text{NH}_4\text{Ac}$  were also used as electrolytes with no outstanding effects noted. It appeared that with the use of the chlorides or nitrates that there was an excessive quantity of liquid corrosion product which escaped either around the reinforcing rod or through places of weakness or porous parts of the specimens. This liquid which was light yellow or brown when it came out, became darker brown or black when exposed to the air or in the electrolyte. Even with the use of an electrolyte the amount of electric current decreased with time. The formation of cracks in the specimens did not appear to result in an increase in the current. The corrosion product on the reinforcing rod may therefore inhibit or restrain the rate of further corrosion.

A second series of tests was conducted in which the 3x6 inch cylinders were placed in tap water with no added salts or electrolyte. Both 110 and 55 volts direct electric current were used. A tabulation of the results are presented in Table 2-9.

With a wet 3x6 inch cylinder made of Type I cement, mix A, and 110v dc, approximately 4 or 5 days were required to cause a crack in the specimen. The electrolytic action was rapid to start and the current decreased with time.

Using tap water, 110 volts, and a wet stored 3x6 inch cylinder made of Type I cement and the B mix, a slight crack was noted at about 50 hours. The crack did not open appreciably in 4 weeks. At 8 weeks the reinforcing rod had corroded and broke off even with the top of the cylinder when the specimen was moved.

With the Type II cement made of the A mix the wet cylinder was found to be cracked in 24 hours at 110 volts in tap water with no added electrolyte.

When dry cylinders made of Types I and II cements, mix A were placed in tap water and 110 volts potential applied, it took about 1 hour for the gas to start coming off the cathode. At 7 hours there was a current of about 0.12 amps for the Type I cement cylinder and 0.50 amps for the Type II cement cylinder. Both cracked in less than 24 hours.

Using only 55 volts and specimens made of Types I and II cements A mix, and tested before drying out, 7 days were required to produce a crack when using only tap water. The current was about 0.33 amps at the start and 0.08 amps at one week. At 3 weeks the cracks had opened up to 1.5 to 2 mm on the surface of the cylinders.

When the specimens made of these cements using the B mix were tested before drying the Type I cylinder cracked in 7 days in tap water and the Type II cylinder in less than 24 hours both with 55 volts potential. The current was about 0.4 amps to start and for the Type I cement specimens only 0.02 amps at 3 weeks although the crack was about 3 mm wide at the surface of the cylinder.

One pair of specimens made of the Types I and II cements, B mix, and air dried were placed in tap water and 110 volt potential applied. No cracks developed in 3 weeks, and the current, which was about 0.13 amps at 24 hours, was only about 0.01 amps after 3 weeks. In these tests a rather large quantity of liquid corrosion product came out near the reinforcing rod of the cylinder made of the Type II cement. The amount of corrosion product extruded when no electrolyte was added to the tap water appeared to be less than when an electrolyte was added.

#### Plans for Future Work

Additional tests of electrolytic corrosion of reinforcing steel in 6x12 concrete cylinders will be performed. A few reinforced concrete beams will be made, cured, and tested when the facilities in the new laboratory are operational.

Table 2-1 - Time for failure or the change in resonance frequency in 6 months of 1:3 (cement to sand) mortars made of Type I cement when stored in solutions of the various reagents.

Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
none	--	+ 50	--	+ 150
$\text{Na}_2\text{SO}_4$	18	--	--	- 100
$\text{MgSO}_4$	--	- 430	--	+ 190
Stearic acid	--	+ 30	--	+ 110
$(\text{NH}_4)_2\text{SO}_4$	18	--	18	--
$\text{NH}_4\text{NO}_3$	4	--	3	--
$\text{Na}_2\text{S}_2\text{O}_3$	--	+ 10	--	+ 250
Cane sugar	--	+ 180	--	+ 120
$\text{NaHSO}_4$	22*	--	24*	--
$\text{K}_2\text{SO}_4$	24*	--	24*	--
$(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4$	22*	--	--	- 30
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	5	--	3	--
KAc	--	+ 10	--	+ 40
$\text{NH}_4\text{Cl}$	3	--	6	--
$\text{Na}_2\text{SO}_3$	--	+ 180	--	+ 300
$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	24*	--	24*	--
Citric acid	**	--	**	--
$\text{NaHSO}_3$	24*	--	--	-1020
$\text{NH}_4\text{Ac}$	--	- 990	22	--
NaAc	--	+ 40	--	+ 130
$\text{Fe}_2(\text{SO}_4)_3$	--	- 100	--	+ 50
$\text{KAl}(\text{SO}_4)_2$	--	- 130	--	+ 120
$\text{KHSO}_4$	--	-1290	--	- 330
$\text{CuSO}_4$	--	+ 70	--	+ 190
$(\text{NH}_4)_2\text{SO}_4$ & sugar	--	- 210	--	+ 60
$\text{KAl}(\text{SO}_4)_2$ & sugar	--	+ 100	--	+ 200
$\text{CaCl}_2$	--	- 220	--	+ 70
Lactic acid***	--	- 880	--	- 460
$\text{K}_2\text{S}_2\text{O}_5$ ***	22	--	--	- 120
PDGA (Monsanto)***	--	- 260	--	- 80
Oleic acid***	--	**	--	**

\* Cracks in specimens noted prior to these measurements.  
 \*\* Surface attack was the dominant feature, causing loss of weight.  
 \*\*\* Measurements made at 5 months, the 6 month values not available at time table was prepared.

Table 2-2 - Time for failure or the change in resonance frequency in 6 months of 1:5 (cement to sand) mortars made of Type I cement when stored in solutions of the various reagents

Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
none	--	+ 20	--	+ 310
Na <sub>2</sub> SO <sub>4</sub>	6	--	7	--
MgSO <sub>4</sub>	22	--	--	+ 490
Stearic acid	--	- 10	--	+ 260
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2	--	6	--
NH <sub>4</sub> NO <sub>3</sub>	2	--	2	--
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	--	- 190	--	+ 170
Cane sugar	--	+ 130	--	+ 140
NaHSO <sub>4</sub>	18	--	18	--
K <sub>2</sub> SO <sub>4</sub>	4	--	5	--
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·FeSO <sub>4</sub>	22*	--	--	+ 190*
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3	--	3	--
KAc	--	- 280	--	+ 40
NH <sub>4</sub> Cl	3	--	5	--
Na <sub>2</sub> SO <sub>3</sub>	22	--	24	--
NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	18	--	24*	--
Citric acid	**	--	**	--
NaHSO <sub>3</sub>	18	--	18	--
NH <sub>4</sub> Ac	4	--	4	--
NaAc	--	- 120	--	+ 60
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	--	- 100	--	+ 320
KAl(SO <sub>4</sub> ) <sub>3</sub>	22	--	--	+ 470
KHSO <sub>4</sub>	12	--	24	--
CuSO <sub>4</sub>	--	0	--	+ 380
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> & sugar	7	--	--	- 40
KAl(SO <sub>4</sub> ) <sub>2</sub> & sugar	--	- 130	--	+ 350
CaCl <sub>2</sub>	--	- 270	--	+ 190
Lactic acid***	--	- 960	--	- 220
K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> ***	12	--	16	--
PDGA (Monsanto)***	--	- 320	--	- 180
Oleic acid***	--	**	--	**

\* Cracks in specimens noted prior to these measurements.  
 \*\* Surface attack was the dominant feature, causing loss of weight.  
 \*\*\* Measurements made at 5 months, the 6 month values not available at time table was prepared.

Table 2-3 - Time for failure or the change in resonance frequency in 6 months of 1:3 (cement to sand) mortars made of Type II cement when stored in solutions of the various reagents

Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
none	--	+ 240	--	+ 140
Na <sub>2</sub> SO <sub>4</sub>	--	+ 190	--	+ 180
MgSO <sub>4</sub>	--	+ 40	--	+ 210
Stearic acid	--	+ 70	--	+ 160
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	--	- 300	--	+ 30
NH <sub>4</sub> NO <sub>3</sub>	--	- 570	--	- 580
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	--	+ 100	--	+ 140
Cane sugar	--	+ 140	--	+ 60
NaHSO <sub>4</sub>	--	- 110	--	+ 20
K <sub>2</sub> SO <sub>4</sub>	--	+ 110	--	+ 200
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> FeSO <sub>4</sub>	--	- 20	--	+ 90
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	--	- 744	--	-1020
KAc	--	+ 10	--	- 10
NH <sub>4</sub> Cl	12	--	--	- 960
Na <sub>2</sub> SO <sub>3</sub>	--	+ 207	--	+ 200
NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	24*	--	24*	--
Citric acid	**	--	**	--
NaHSO <sub>3</sub>	--	+ 20	--	+ 100
NH <sub>4</sub> Ac	--	- 890	--	- 520
NaAc	--	+ 10	--	+ 60
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	--	+ 130	--	+ 120
KFe(SO <sub>4</sub> ) <sub>3</sub>	--	+ 10	--	+ 190
KHSO <sub>4</sub>	--	- 400	--	- 70
CuSO <sub>4</sub>	--	+ 130	--	+ 180
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> & sugar	--	- 200	--	+ 40
KAl(SO <sub>4</sub> ) <sub>2</sub> & sugar	--	+ 130	--	+ 280
CaCl <sub>2</sub> ***	--	- 120	--	+ 30
Lactic acid ***	--	- 500	--	- 420
K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> ***	--	- 50	--	+ 130
PDGA (Monsanto) ***	--	- 240	--	- 100
Oleic acid ***	--	**	--	**

\* Cracks in specimens noted prior to these measurements.  
 \*\* Surface attack was the dominant feature, causing loss of weight.  
 \*\*\* Measurements made at 5 months, the 6 month values not available at time table was prepared.

Table 2-4 - Time for failure or the change in resonance frequency in 6 months of 1:5 (cement to sand) mortars made of Type II cement when stored in solutions of the various reagents

Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
none	--	+ 100	--	+ 220
$\text{Na}_2\text{SO}_4$	--	+ 160'	--	+ 370
$\text{MgSO}_4$	--	+ 340	--	+ 470
Stearic acid	--	+ 60	--	+ 160
$(\text{NH}_4)_2\text{SO}_4$	5	--	--	- 410
$\text{NH}_4\text{NO}_3$	--	- 720	--	- 730
$\text{Na}_2\text{S}_2\text{O}_3$	--	- 70	--	+ 90
Cane sugar	--	+ 100	--	- 30
$\text{NaHSO}_4$	--	+ 30	--	+ 170
$\text{K}_2\text{SO}_4$	--	+ 230	--	+ 370
$(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4$	--	+ 50	--	+ 180
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	--	- 780	--	- 150
KAc	--	- 260	--	+ 60
$\text{NH}_4\text{Cl}$	2	--	3	--
$\text{Na}_2\text{SO}_3$	--	+ 240	--	+ 380
$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	24*	--	24*	--
Citric acid	**	--	**	--
$\text{NaHSO}_3$	--	- 754	--	+ 268
$\text{NH}_4\text{Ac}$	2	--	4	--
NaAc	--	- 130	--	- 120
$\text{Fe}_2(\text{SO}_4)_3$	--	+ 100	--	+ 200
$\text{KFe}(\text{SO}_4)_3$	--	+ 180	--	+ 300
$\text{KHSO}_4$	--	- 110	--	- 50
$\text{CuSO}_4$	--	+ 150	--	+ 240
$(\text{NH}_4)_2\text{SO}_4$ & sugar	8	--	--	- 540
$\text{KAl}(\text{SO}_4)_2$ & sugar	--	+ 120	--	+ 180
$\text{CaCl}_2$ ***	--	- 210	--	+ 60
Lactic acid ***	--	- 790	--	- 240
$\text{K}_2\text{S}_2\text{O}_5$ ***	--	- 190	--	+ 250
PDGA (Monsanto) ***	--	- 170	--	- 210
Oleic acid ***	--	**	--	**
* Cracks in specimens noted prior to these measurements. ** Surface attack was the dominant feature, causing loss of weight. *** Measurements made at 5 months, the 6 month values not available at time table was prepared.				

Cement to sand ratio	1:3	1:3	1:3	1:3	1:3	1:3	1:5	1:5	1:5	1:5
Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry	Dry	Moist	Moist	Dry	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Moist	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Change in resonance frequency cps
NH <sub>4</sub> Ac	1*	--	1*	--	1*	--	--	1*	--	--
MgSO <sub>4</sub>	--	+ 50	--	+ 70	--	--	- 60	--	+ 180	+ 180
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	--	- 910*	--	- 335	2	--	--	--	- 660	- 660
Na <sub>2</sub> SO <sub>4</sub>	--	- 230*	--	+ 120	6*	--	--	12	--	--
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	--	+ 140	--	+ 45	--	--	-1120	--	- 360	- 360
CaCl <sub>2</sub>	8	--	6	--	4	--	--	6	--	--
NH <sub>4</sub> NO <sub>3</sub>	--	- 240	--	+ 30	12	--	--	3*	--	--
K <sub>2</sub> SO <sub>4</sub>	--	- 400	--	+ 120	4	--	--	4	--	--
NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	--	--	--	+ 240	--	--	--	10	--	--
* Severe cracking in the specimens noted prior to these measurement.										

Table 2-5 - Time for failure, or change in dynamic modulus in 18 weeks of mortars of Type I cement when stored on end in shallow concentrated solutions of the various reagents.



Cement to sand ratio	1:3	1:3	1:3	1:3	1:3	1:5	1:5	1:5
Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry	Moist	Moist	Dry	Dry
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
$\text{NH}_4\text{Ac}$	1*	--	1*	--	1*	--	1*	--
$\text{MgSO}_4$	--	- 10	--	+ 30	--	- 40	--	+ 150
$(\text{NH}_4)_2\text{SO}_4$	--	- 690	--	- 380	2	--	--	-1080
$\text{Na}_2\text{SO}_4$	--	+ 80	--	+ 160	18	--	18	--
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	--	+ 60	--	+ 80	18	--	--	- 110
$\text{CaCl}_2$	6	--	6	--	6	--	6	--
$\text{NH}_4\text{NO}_3$	--	- 80	--	- 10	3	--	2	--
$\text{K}_2\text{SO}_4$	--	- 80	--	+ 10	--	- 40	--	+ 210
$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	--	--	--	+ 890	--	--	--	- 30
* Severe cracking in the specimens noted prior to these measurements.								

Table 2-6 - Time for failure, or change in dynamic modulus in 18 weeks of mortars made of Type II cement when stored on end in shallow concentrated solutions of the various reagents.



Concrete Mix	A	A	A	A	A	B	B	B	B	C	C
Condition of Specimen at Start of Test	Moist	Moist	Dry	Dry	Moist	Moist	Dry	Dry	Moist	Moist	Moist
Reagent	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks
none	--	+ 120	--	+ 680	--	+ 110	--	+ 710	--	+ 160	--
NH <sub>4</sub> NO <sub>3</sub>	13	--	14	--	4	--	5	--	13	--	--
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5	--	7	--	6	--	19	--	10	--	--
NH <sub>4</sub> Cl	16	--	19	--	7	--	7	--	10	--	--
CaCl <sub>2</sub>	--	+ 2	--	+ 560	--	- 150	--	+ 450	--	- 70	--
MgSO <sub>4</sub>	--	+ 180	--	+ 550	--	- 350	--	+ 450	--	+ 80	--
K <sub>2</sub> SO <sub>4</sub>	19*	--	15*	--	15*	--	12	--	--	- 490	--
Na <sub>2</sub> SO <sub>4</sub>	19*	--	9*	--	7*	--	4*	--	--	+ 30	--
NH <sub>4</sub> Ac	--	--	24	--	--	--	7	--	24	--	--
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	6*	--	12*	--	6	--	16*	--	6*	--	--
* Failed by bad spalling.											

Table 2-7 - Time for failure, or change in resonance frequency in 24 weeks of 3x6 inch concrete cylinders made of Type I cement when stored in solutions of the various reagents.

Concrete Mix	A		A		A		B		B	
Condition of Specimen at Start of Test	Moist	Time for failure, weeks	Change in resonance frequency cps	Moist	Dry	Change in resonance frequency cps	Moist	Time for failure, weeks	Moist	Dry
Reagent	Time for failure, weeks	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Time for failure, weeks	Change in resonance frequency cps	Time for failure, weeks	Change in resonance frequency cps
none	--	--	+ 130	--	+ 590	--	--	+ 160	--	+ 860
NH <sub>4</sub> NO <sub>3</sub>	--	--	- 800	--	-1400	19	--	--	2	--
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	13	2	--	2	--	--	--	- 910	--	- 380
NH <sub>4</sub> Cl	19	16	--	16	--	11	--	--	9	--
CaCl <sub>2</sub>	--	--	- 60	--	+ 370	--	--	- 240	--	+ 430
MgSO <sub>4</sub>	--	--	+ 100	--	+ 480	--	--	+ 110	--	+1070
K <sub>2</sub> SO <sub>4</sub>	--	--	+ 170	--	+ 600	--	--	+ 80	--	+ 640
Na <sub>2</sub> SO <sub>4</sub>	--	--	+ 190	--	+ 640	--	--	+ 100	--	+ 270
NH <sub>4</sub> Ac	--	--	--	--	-1340	13	--	--	10	--
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	16*	--	--	--	+ 140	--	--	- 990	--	+1360
* Failed by bad spalling.										

Table 2-8 - Time for failure, or change in resonance frequency in 24 weeks of 3x6 inch concrete cylinders made of Type II cement stored in solutions of the various reagents

Type of cement	Concrete mix	Condition at Start of Test	Applied voltage	Time at which crack was noted, days
I	A	moist	110	5
I	B	moist	110	2
II	A	moist	110	1
I	A	dry	110	1
II	A	dry	110	1
I	B	dry	110	—*
II	B	dry	110	—*
I	A	moist	55	7
II	A	moist	55	7
I	B	moist	55	7
II	B	moist	55	1
* No cracks had developed in 3 weeks.				

Table 2-9 - Time of cracking of 3x6 inch concrete cylinders having 3/8 inch reinforcing rod in the principal axis with an applied direct electrical current



### DISTRIBUTION LIST

a. Twenty copies of the report shall be forwarded to Defense Documentation Center Headquarters, Attention: DDC-IRS, Cameron Station, Alexandria, Virginia 22314.

b. Twenty-three copies of the report shall be forwarded to Commanding Officer, U. S. Army Edgewood Arsenal, Attention: SMUEA-RCRP, Research Laboratories, Mr. Gordon N. Jarman, Project Officer, Edgewood Arsenal, Maryland 21010.

## DOCUMENT CONTROL DATA - R&amp;D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) NATIONAL BUREAU OF STANDARDS, Washington, D. C. 20234		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE  INDUCED ACCELERATED DETERIORATION OF PORTLAND CEMENT CONCRETE			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Semiannual Report - July-December 1966			
5. AUTHOR(S) (Last name, first name, initial)  Blaine, Raymond L.			
6. REPORT DATE 9 January 1967		7a. TOTAL NO. OF PAGES (complete)	7b. NO. OF REFS None
8a. CONTRACT OR GRANT NO. D018-0-35-A6-02806		9a. ORIGINATOR'S REPORT NUMBER(S)  SEMIAPR, NBS Report 9465	
b. PROJECT NO. US Army Ballistics Research Laboratories		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)  None	
10. AVAILABILITY/LIMITATION NOTICES  This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Md. 21010			
11. SUPPLEMENTARY NOTES  Mortars		12. SPONSORING MILITARY ACTIVITY US Army Ballistics Research Laboratories Aberdeen Proving Ground, Maryland 21008	
13. ABSTRACT Measurements made of the effects of various salt solutions on the fundamental resonance frequencies of mortar and concrete specimens made of two portland cements indicated that ammonium salts appeared most aggressive when specimens were completely immersed. The specimens made of the Type II cement were more resistant to attack (especially by the sulfates) than those made of the Type I cement, and the richer mixes were more resistant than the leaner mixes. Some specimens failed in some solutions in 2 weeks but in other solutions comparable specimens were stronger after 6 months of storage than at the start of the test. Ammonium acetate caused the most rapid deterioration on mortars stored on end in a shallow concentrated solution. Other salts also caused fairly rapid deterioration of the mortar specimens with this test condition. Using 110 volt direct electric current to cause corrosion of reinforcing steel, caused cracking of 3 x 6 inch concrete cylinders in less than 24 hours to 7 days even without the use of an electrolyte. In some instances the corrosion product was extruded and no cracking occurred. The amount of current decreased with time of application of the applied potential.			

#### 14. KEYWORDS

Deterioration  
Concrete cylinders  
Mortar bars  
Corrosion  
Reinforced steel  
Aggressive chemicals  
Electrochemical corrosion  
Portland cement concrete  
Acceleration  
Cement<sup>1</sup>  
Absorption  
Evaporation  
Crystal formation  
Disintegration





## THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards<sup>1</sup> provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

**THE INSTITUTE FOR BASIC STANDARDS** . . . provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics<sup>2</sup>—Radio Standards Laboratory,<sup>2</sup> which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

**THE INSTITUTE FOR MATERIALS RESEARCH** . . . conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics<sup>2</sup>—Materials Evaluation Laboratory—Office of Standard Reference Materials.

**THE INSTITUTE FOR APPLIED TECHNOLOGY** . . . provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Textile and Apparel Technology Center—Technical Analysis—Center for Computer Sciences and Technology—Office of Weights and Measures—Office of Engineering Standards Services—Office of Invention and Innovation—Clearinghouse for Federal Scientific and Technical Information.<sup>3</sup>

<sup>1</sup> Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

<sup>2</sup> Located at Boulder, Colorado, 80302.

<sup>3</sup> Located at 5285 Port Royal Road, Springfield, Virginia, 22151.

